

PATENT SPECIFICATION

(11) 1 591 741

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- (21) Application No. 44077/77 (22) Filed 24 Oct. 1977
(31) Convention Application No. 742023
(32) Filed 15 Nov. 1976 in
(33) United States of America (US)
(44) Complete Specification published 24 June 1981
(51) INT CL³ C08F 2/50 C08K 3/34
(52) Index at acceptance

C3V BF
C3W 201 225
C3Y B120 B123 B230 B248 H660



(54) IMPROVEMENTS IN OR RELATING TO PASTE-LIKE, PHOTOPOLYMERIZABLE, DENTAL RESTORATIVE COMPOSITIONS

(71) We, SYBRON CORPORATION, of 1100 Midtown Tower, Rochester, New York 14604, United States of America, a corporation organized and existing under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to paste-like, photopolymerizable, dental restorative compositions.

Known photopolymerizable, dental restorative compositions have contained thermosetting acrylic esters of bis-phenolic compounds, an acrylic monomer diluent and a combination of a photopolymerization initiator and an accelerator. As a rule, compositions of this nature are two-part systems. U.S. Patent Specification 3,709,866 describes one such system, where one component containing the initiator is kept separate from the rest of the composition and the two components are mixed by the dentist in a definite proportion just prior to use. This procedure is necessary in order to maintain a certain shelf life for these dental materials. With such a mix, homogeneity is almost impossible to achieve when, in use, a drop of the component containing the initiator is mixed with an almost solid composite component containing the rest of the composition. Failure to produce a homogenous mix may create irregularities within the restoration. U.S. Patent Specification 3,759,807 discloses the use of a combination of an organic carbonyl compound and an amine, more particularly, the combination of benzophenone and a tertiary amine as the initiator and accelerator, respectively. Although these compositions are polymerizable, they cannot be used as filling material for dental cavities because of their slow curing. Dental composite systems, containing a derivative of the diglycidyl ether of bisphenol A, an acrylic binder and a filler, which in use are cross-linked with benzoyl peroxide or some other suitable catalyst, are disclosed in U.S. Patent Specification 3,539,533. The resultant compositions are stated to have a compression strength of only 26000 psi, however. Further, currently available dental composite materials are characterized by being systems having two part, for instance, paste-paste, paste-liquid, liquid-liquid or power-liquid. The two parts are mixed together in certain prescribed proportions. The properties of the final product depend upon how well and how fast the mixing is carried out. In mixing the two parts, air becomes incorporated into the composition. This air acts as a polymerization inhibitor, produces mechanical flaws in the restorative material and also is slow curing. Further, non-uniform mixing may lower the quality of the fillings. This deficiency is completely eliminated by the present invention, which provides a one part system.

It has now been found that uniform one-part photopolymerizable, dental restorative compositions can be made, which are highly suitable for use as dental filling compositions and which furthermore have the considerable additional advantages of a long shelf life and of not requiring hand mixing or activation by the dentist prior to use.

According to this invention, there is provided a one part, paste-like, photopolymerizable, dental restorative composition which comprises:

- (a) an ethylenically unsaturated monomer;

(b) a diluent monomer copolymerizable with the ethylenically unsaturated monomer;

(c) a photo-initiator for photo-initiating the copolymerization of the ethylenically unsaturated and diluent monomers;

(d) an accelerator for accelerating the photo-initiation of the copolymerization of the ethylenically unsaturated and diluent monomers; and

(e) an inorganic filler comprising barium aluminium silicate and/or lithium aluminium silicate.

The composition can be used as a pit and fissure sealant, a bonding agent, a cavity liner and a restoration glaze.

According to a preferred embodiment of such a composition, the filler advantageously represents up to 85% by weight of the composition.

Preferably, also, the composition is polymerizable by radiation of a wavelength in the range from 3600 to 4500 Å. The compositions of the invention thus have the highly desirable and advantageous characteristic that in use, which involves no mixing or measuring of separate components, the only operations needed are, essentially, application and illumination with radiation of the appropriate wavelength.

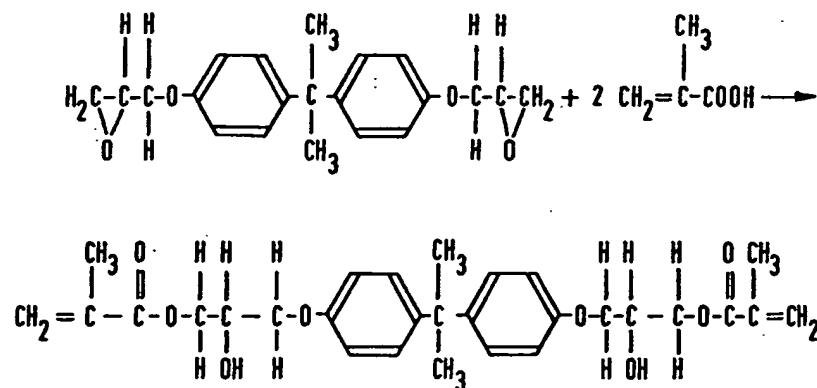
Advantageously, the photo-initiator comprises an alpha-diketone or a derivative thereof, and the accelerator, an amine.

Photopolymerizable compositions have been used increasingly in recent years as restorative materials for filling dental cavities. The present invention can be regarded as providing improved compositions of this general class, which are of a one part form and so provide all the attendant advantages, while at the same time being curable in essentially the same way as other, more complex photopolymerizable systems.

In the one part compositions of the invention, the ethylenically unsaturated monomer typically comprises unsaturated sites which are capable of undergoing polymerization, while the main purpose of the diluent monomer is to control the viscosity of the other monomer.

The purpose of the photo-initiator is to produce free radicals in the composition, on exposure to radiation, which then react with the double bonds of the monomer unsaturation to initiate polymerization, while the accelerator is, of course, present for the purpose of increasing the speed of photopolymerization of the composition. The filler or filler combination is selected so as to give the composition the desired physical characteristics and other properties, particularly after use and particularly in relation to appearance.

The ethylenically unsaturated monomer preferably used in the preparation of a one part, paste-like composition of this invention, advantageously is derived from the reaction of the diglycidyl ether of bisphenol A with methacrylic acid or acrylic acid, which, in the case of the methacrylic monomer, may be represented as:



The resulting glycidyl methacrylate derivative of bisphenol A is known as bisphenol A - bis(3 - methacrylate - 2 - hydroxypropyl)ether. In relation to the present invention, this monomer serves as a binder for the photopolymerizable dental composition and for convenience it is referred to below as "bis-GMA". modifications of this monomer can also be used in carrying out this invention.

The diluent monomer used is preferably a mono-, di- or trifunctional acrylate or methacrylate and is advantageously selected from alkyl methacrylates, alkylene dimethacrylates, trimethacrylates, alkyl acrylates, alkylene diacrylates and triacrylates. Especially suitable diluent monomers include:

- 5 methylmethacrylate
- ethylmethacrylate
- butylmethacrylate
- n* - propylmethacrylate
- isopropylmethacrylate
- 10 1,3 - butylenedimethacrylate
- ethyleneglycolmonomethacrylate
- ethyleneglycoldimethacrylate
- triethyleneglycoldimethacrylate
- 1,6 - hexaneglycoldiacrylate
- 15 tetraethyleneglycoldiacrylate and
- tetramethyleneglycoldimethacrylate.

One or more of these monomers can be used in formulating a photopolymerizable composition. The diluent monomers copolymerize with the bis-GMA or other ethylenically unsaturated monomer on exposure to radiation in the presence of the photo-initiator and accelerator.

- Another component desirably present in the composition is a polymerization inhibitor, which prevents premature polymerization of the bis-GMA or other ethylenically unsaturated monomer and the diluent monomer and is present only in small quantities. Suitable polymerization inhibitors include hydroquinone (HQ), the methyl ether of hydroquinone (MEHQ), butylated hydroxytoluene (BHT) and triphenylstyrene. Desirably, the polymerization inhibitor is present and it is preferable for obvious reasons for such a material to be incorporated in both monomers before either is used in formulating the one part paste-like compositions of the invention. References to both the monomers are to be taken as meaning (unless otherwise specified) either the respective ingredient *per se* or such ingredient in admixture with any appropriate polymerization inhibitor. Where either of the polymerizable ingredients contains MEHQ or some other polymerization inhibitor, it is present in small quantities, for instance 100 ppm, 200 ppm or some lesser or greater effective amount, and thus becomes incorporated in the photopolymerizable composition of the invention.

Photo-initiators generally are photosensitive carbonyl compositions. The initiators most preferably used in this invention are alpha-diketones and their derivatives, particularly those having the general formula:



- 40 where R and R' are the same or different and each represents an aliphatic or aromatic group and their derivatives. Examples of suitable photo-initiators are:

| | Formula | |
|------------------------|------------------------------|----|
| biacetyl | $CH_3COCOCH_3$ | |
| 2,3 - pentanedione | $CH_3COCOCH_2CH_3$ | |
| 45 benzil | $C_6H_5COCOC_6H_5$ | 45 |
| 4,4' - dimethoxybenzil | $CH_3OC_6H_4COCOC_6H_4OCH_3$ | |
| 4,4' - oxydibenzil | $(C_6H_5COCOC_6H_5)_2O$ | |

These photo-initiators are slightly yellow in colour. Since they are present in small quantities, however, the final polymerized product is almost colourless.

- 50 Photo-accelerators are chemical compounds which, in the presence of an initiator, accelerate the photoreaction. In practice, therefore, an accelerator helps the polymerization to penetrate throughout a restoration, even one which is placed in a deep cavity. The preferred accelerators, in the context of this invention, are amines, whether primary, secondary or tertiary with the latter being those most preferred, and also, diamines. Examples of preferred amines include dimethylparatoluidine, N,N' - dimethylbenzylamine, N - methyl dibutylamine, triethylamine and trihexylamine. Examples of preferred diamines include N,N,N',N' - tetraethyl - ethylenediamine and N,N,N',N' - tetramethyl - 1,6 - hexanediamine.

- 60 In the absence of the previously-mentioned photo-initiators, these amines do not function to induce photopolymerization. Even though all amines, in combination

with the previously-mentioned photo-initiators, accelerate the reaction to some extent, the tertiary amines (e.g. triethylamine and trihexylamine) are found to be the best for causing polymerization deep into the composite mass. Amines with aromatic groups are generally undesirable, because they impart a slight colour to the composition, on prolonged exposure to light.

When a combination of benzophenone and an amine, known in the prior art, is used in a bis-GMA system, either polymerization is not caused or the system is very slow curing. It has been found that the combination of an alpha-diketone as the photo-initiator with an amine as the polymerization accelerator, using actinic radiation as the polymerization activator, produces a filling having a high crushing strength.

At least 25% of the filler is preferably barium aluminium silicate, although up to 100% can be used, if so desired. The presence of this filler imparts to the restored material sufficient radio-opacity so that it contrasts well with tooth tissue, provided a minimum of 6.5% barium oxide is present in the composition. The particle size distribution of these fillers may range from less than 5 to approximately 40 microns. The bonding between the silicate fillers and the organic matrix material is increased when the fillers are used in a silanated form. Preferred silane bonding agents have any of the general formulae $RSiX_3$, R_2SiX_2 and R_3SiX , where X represents a halogen atom or an alkoxy or hydroxy group and R represents a vinyl, methacrylate, allyl, methallyl itaconate, maleate, acrylate, itaconate, maleate acrylate aconitate, fumarate, alkyl, aryl, alkenyl crotonate, cinnamate, citraconate, sorbate or glycidyl group. When silanation is complete, a monomolecular coating of the bonding agent is present on the filler surface, which improves its adhesion to the resin matrix.

The dental restorative composition of the invention is polymerized by exposing it to an activator, i.e. an energy source which activates a photoreaction. A suitable source of actinic radiation, for use in carrying out this invention, is for instance an ultraviolet diagnostic lamp, e.g. that manufactured by Blank Light Eastern, a division of Spectronics Corp. of Westbury, Long Island, New York and designated the "Spectroline B-100". This is a 100 watt high-pressure mercury vapour lamp having a radiation wavelength capacity of 3200 to 4200 Å. The spot bulb used in this lamp is cooled by a fan. An average amount of the dental filling material, i.e. 0.2 to 0.3 gm, was polymerized completely by irradiation with the above lamp for 20—30 seconds when the material was kept 4 inches away from the lamp. Under these conditions, the material polymerized to a depth of about 2 mm.

A preferred formulation of the composition of the invention contains the various ingredients in the following ranges of amounts:

| | | Parts by weight | |
|----|---|-----------------|----|
| 40 | Ethylenically unsaturated monomer (including inhibitor) | 10—25 | 40 |
| | Diluent monomer (including inhibitor) | 2—5 | |
| | Photo-initiator, e.g. alpha-diketone or its derivative | 0.001—1 | |
| | Accelerator, e.g. amine | 0.01—2 | |
| | Filler | 70—85 | |

45 The dental restorative composition of the invention is preferably made up as follows:

The ethylenically unsaturated monomer was mixed with the diluent monomer, the photo-initiator and the accelerator. These were mixed together well in a glass vessel by means of a rod of a non-stick material, such as, "Teflon" (Registered Trade Mark). When the mixture was fairly uniform, barium aluminium silicate was added and mixed in well. Finally, the rest of the filler was added in three or four instalments and mixed in well. The resultant material was stored for one week before testing. The resultant well-mixed heavy paste was packed in a split cylindrical polytetrafluoroethylene mould, 12.5 mm high by 6 mm in diameter and open at both ends. The top and bottom were covered with strips of film, such as "Mylar" (Registered Trade Mark) film and pressed to give a smooth surface. The "Mylar" film covered ends were then exposed for 15 seconds each to the light emitted from a "Spectroline B-100" lamp at a distance of 4 inches. The split mould was then opened and each side of the specimen was exposed to actinic radiation for 15 seconds. The total exposure time was one minute. After 10 minutes ageing, the polymerized composition was tested and found to have a strength ranging from 27,000 to 33,000 psi. The strength increased to 40,000 if the cured sample was aged for two weeks. On prolonged ageing, the strength reached 45,000 psi.

EXAMPLE I

| | | Percent by weight | |
|----|--|-------------------|----|
| 5 | bis-GMA monomer (including MEHQ 200 ppm) | 18 | |
| | methyl methacrylate (including MEHQ 100 ppm) | 3 | 5 |
| | 4,4' - oxydibenzil | 0.2 | |
| | triethylamine | 0.2 | |
| | barium aluminium silicate | 23 | |
| | lithium aluminium silicate | 55.6 | |
| 10 | This composition was prepared by the method described previously and the strength of the polymerized material, after exposure to a "Spectroline B-100" lamp, was determined. Upon a half minute exposure the strength of the material became 25,000 psi, after one minute exposure it was 30,000 psi and after 5 minutes exposure it was 36,700 psi. | | 10 |

EXAMPLE II

| EXAMPLE II | | Percent by weight | | |
|------------|---|-------------------|----|----|
| | bis-GMA monomer (including MEHQ 200 ppm) | 18 | | |
| 20 | 1,3 - butylene dimethacrylate (including MEHQ 50 ppm) | 3 | 20 | |
| | 4,4' - dimethoxybenzil | 0.08 | | |
| | N - methylidibutylamine | 0.2 | | |
| | barium aluminium silicate | 23 | | |
| | lithium aluminium silicate | 55.72 | | |
| 25 | The strength of this composition was measured as before. On exposure to a "Spectroline B-100" lamp for 1 minute, it was found to be 30,000 psi. | | | 25 |

EXAMPLE III

| | | Percent by weight | |
|----|---|-------------------|----|
| 30 | bis-GMA monomer (including MEHQ 200 ppm) | | 30 |
| | triethyleneglycoldimethacrylate (including MEHQ 100 ppm) | 3 | |
| | benzil | 0.08 | |
| | N - methylidibutylamine | 0.2 | |
| 35 | barium aluminium silicate | 23 | 35 |
| | lithium aluminium silicate | 55.72 | |
| | The strength of the polymerized material when exposed to a "Spectroline B-100" lamp for a total of 1 minute was 29,500 psi. | | |

EXAMPLE IV

| | | | | |
|----|---|--|--|----|
| 40 | This was a repetition of Example III, except that the diluent monomer was replaced by the same amount of 2 - ethylhexylacrylate. The measured strength on one minute exposure to a "Spectroline B-100" lamp was 32,000 psi. Generally, acrylate monomers are more reactive than methacrylate and dimethacrylate monomers. | | | 40 |
|----|---|--|--|----|

EXAMPLE V

| | | Percent by weight | |
|----|---|-------------------|----|
| 45 | bis-GMA monomer (including MEHQ 200 ppm) | 18 | 45 |
| | methylmethacrylate (including MEHQ 100 ppm) | 3 | |
| | benzophenone | 0.4 | |
| 50 | triethylamine | 0.4 | 50 |
| | barium aluminium silicate | 23 | |
| | lithium aluminium silicate | 55.2 | |
| | No cure was noticed when this mix is exposed to a "Spectroline B-100" lamp for 4 minutes. | | |

EXAMPLE VI

| | | | | |
|----|---|--|--|----|
| 55 | Example V was repeated, but using benzil instead of benzophenone. As usual, the composition was packed into a half-inch mold and exposed to a "Spectroline B- | | | 55 |
|----|---|--|--|----|

100" lamp for a total period of 1 minute. The strength of the polymerized material was 33,000 psi.

EXAMPLE VII

Example V was repeated, but using diphenyl triketone, $C_6H_5COCOCOC_6H_5$, instead of benzophenone. After exposure to a "Spectroline B-100" lamp for a period of one minute, the strength was only 7400 psi.

EXAMPLE VIII

| | | Percent by weight | |
|----|---|-------------------|----|
| 10 | bis-GMA monomer (including MEHQ 200 ppm) | 18 | 10 |
| | methylmethacrylate (including MEHQ 100 ppm) | 3 | |
| | 4,4' - oxydibenzil | .05 | |
| | tetraethylethylenediamine | .09 | |
| | barium aluminium silicate | 23 | |
| 15 | lithium aluminium silicate | 55.86 | 15 |

In this example, where a diamine accelerator was used, the strength of the polymerized material on exposure to a "Spectroline B-100" lamp for a total of 1 minute was 30,000 psi.

EXAMPLE IX

| | | Percent by weight | |
|----|---|-------------------|----|
| 20 | bis-GMA monomer (including MEHQ 200 ppm) | 18 | 20 |
| | methylmethacrylate (including MEHQ 100 ppm) | 3 | |
| | 4,4' - oxydibenzil | 0.2 | |
| 25 | diisopropylamine | 0.2 | 25 |
| | barium aluminium silicate | 23 | |
| | lithium aluminium silicate | 55.6 | |

In this case, a secondary amine was used as the accelerator. After mixing, the composition was packed into a 12.5x6 mm "Teflon" mould as described before. The "Mylar" film covered ends were exposed for 15 seconds each to a "Spectroline B-100" lamp. When the mould was opened, the specimen was broken in the middle, indicating that the reaction was slow. Therefore, the "Mylar" film covered ends were exposed for 30 seconds each and, after opening the mould without affecting the size and shape of the specimen, each side was exposed for another 30 seconds. Thus the total exposure time was 2 minutes. The crushing strength under these conditions was found to be 26,000 psi.

EXAMPLE X

Example IX was repeated with a primary amine, viz. *n* - butylamine. The strength after two minutes exposure to a "Spectroline B-100" lamp was 16,000 psi. This shows that tertiary amines are the most suitable.

EXAMPLE XI

In this example, a different form of ethylenically unsaturated monomer was used. The glycidyl ether of bisphenol A was reacted with glacial acrylic acid and the resultant product, bisphenol-A - bis(3 - acrylate - 2 - hydroxypropyl)ether (bis-AHE), was used to prepare the composite.

| | | Percent by weight | |
|----|---|-------------------|----|
| | bis-AHE (including MEHQ 100 ppm) | 18 | |
| | 1,6 - hexanedioldiacrylate (including HQ 200 ppm) | 3 | |
| 50 | benzil | .08 | 50 |
| | triethylamine | .2 | |
| | barium aluminium silicate | 23 | |
| | lithium aluminium silicate | 55.72 | |

This composition was treated in the same way as before. On exposure to a "Spectroline B-100" lamp for a total of one minute the material had a crushing strength of 31,500 psi.

EXAMPLE XII

The most suitable formulation for dental filling material is given below:

| | | Percent by weight | |
|----|---|-------------------|----|
| 5 | bis-GMA monomer (including MEHQ 200 ppm) | 18 | 5 |
| | 1,6 - hexanedioldiacrylate (including MEHQ 100 ppm) | 2.8 | |
| | benzil | 0.08 | |
| | triethylamine | 0.2 | |
| | barium aluminium silicate | 23 | |
| 10 | lithium aluminium silicate | 55.82 | 10 |

Five pounds of the above mixture was made using a mechanical stirrer and was tested in the same way as before. The polymerized material was found to have a crushing strength of 32,000 psi, after exposure to a "Spectroline B-100" lamp for a total of 1 minute.

15 The latter composition was aged in the dark for more than three years at room temperature and tested again. It duplicated the curing and strength characteristics of the fresh material. This confirmed the long shelf life of the product.

20 Since dentists can use the compositions of the invention without any additions or mixing steps, restorations essentially free of occluded air bubbles are possible. This eliminates a great deal of mechanical defects and improves finishing of the restoration to give a smoother solid surface. A smooth surface is less prone to staining as well as bacterial accumulation and gives a smooth feel to the tongue.

25 Radiation of a wavelength from 2970 to 3200 Å is capable of causing cutaneous sunburn and of carcinogenesis. This narrow band is responsible for so-called "photo-toxic reactions". The polymerization reaction was repeated after filtering the radiation completely up to 3200 Å. No change in strength of the polymer was observed.

30 By interposing different optical filters between the lamp and the material, it was found that the most effective polymerization occurred with light having a wavelength of 4000—4500 Å, i.e. the visible region.

The cure test was repeated with a tungsten-halogen lamp as a source of visible light, manufactured by General Electric Co. The light was focussed on the material through a 6" fibre bundle. It was found that the material cured more effectively with the tungsten-halogen lamp than with a mercury lamp.

35 Though the best modes are described herein, variations in the formulae are possible. An increase in the quantity of diluent reduces the viscosity. An increase in the filler quantity increases the strength, but thickens the paste. Strength is also increased, with increase in the quantity of benzil. Too much benzil should be avoided, since it imparts a yellow colour and may cause polymerization if the material is exposed to incident light. The initiator and accelerator composition described can be used to photopolymerize a variety of ethylenically unsaturated monomers.

40 Thus, the composition of the invention gives an option to dentists to use sufficiently powerful visible light to polymerize the material and so to avoid the potential risk involved in using ultraviolet light (Journal of American Dental Association, Vol. 92, April 1976).

WHAT WE CLAIM IS:—

1. A one part, paste-like, photopolymerizable, dental restorative composition comprising:
 - 50 (a) an ethylenically unsaturated monomer;
 - (b) a diluent monomer copolymerizable with the ethylenically unsaturated monomer;
 - (c) a photo-initiator for photo-initiating the copolymerization of the ethylenically unsaturated and diluent monomers;
 - 55 (d) an accelerator for accelerating the photo-initiation of the copolymerization of the ethylenically unsaturated and diluent monomers; and
 - (e) an inorganic filler comprising barium aluminium silicate and/or lithium aluminium silicate.
2. A composition according to Claim 1, wherein the inorganic filler comprises at least 6.5%, by weight of the composition, of barium oxide.
- 60 3. A composition according to Claim 1 or 2, wherein the inorganic filler comprises up to 85% by weight of the composition.

4. A composition according to Claim 1, 2 or 3, wherein the ethylenically unsaturated monomer is bis-GMA.
5. A composition according to any preceding claim wherein the diluent monomer is a mono-, di- or trifunctional acrylate or methacrylate.
- 5 6. A composition according to Claim 5, wherein the diluent monomer is 1,6 - hexaneglycoldiacrylate.
7. A composition according to any preceding claim, wherein the photo-initiator is an alpha-diketone or a derivative thereof.
- 10 8. A composition according to Claim 7, wherein the alpha-diketone is benzil.
9. A composition according to any preceding claim, wherein the accelerator is an amine.
- 10 10. A composition according to Claim 9, wherein the accelerator is a tertiary amine.
11. A composition according to Claim 10, wherein the tertiary amine is trihexylamine.
- 15 12. A composition according to Claim 1 or any of Claims 3 to 11, when dependent upon Claim 1, wherein the proportions by weight of the ingredients are:
- | | | | |
|----|-----------------------------------|---------|----|
| | Ethylenically unsaturated monomer | 10—25 | |
| | Diluent monomer | 2—5 | |
| 20 | Photo-initiator | 0.001—1 | 20 |
| | Accelerator | 0.01—2 | |
| | Barium aluminium silicate | 0—85 | |
| | Lithium aluminium silicate | 0—85 | |
13. A composition according to Claim 12, comprising:
- | | | | |
|----|---|-------|----|
| 25 | bis-GMA resin (including MEHQ 200 ppm) | 18 | 25 |
| | 1,6 - hexanedioldiacrylate (including MEHQ 100 ppm) | 2.8 | |
| | benzil | 0.08 | |
| | trihexylamine | 0.2 | |
| | barium aluminium silicate | 23 | |
| 30 | lithium aluminium silicate | 55.82 | 30 |
14. A composition according to any preceding claim which is polymerizable by radiation of a wavelength in the range from 3600 to 4500 Å.
15. A composition according to any of Claims 1 to 13 which is polymerizable by actinic radiation.
- 35 16. A composition according to Claim 15, wherein the actinic radiation has a wavelength in the range from 3200 to 4200 Å.
17. A composition according to any preceding claim comprising a polymerization inhibitor.
18. A composition according to any preceding claim, in which the filler is in silanated form.
- 40 19. A one part, paste-like photopolymerizable dental restorative composition according to Claim 1, substantially as described with reference to any of the foregoing Examples I to IV, VI and VIII to XII.

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